ATOMIC LAYER DEPOSITION OF NOBLE METALS

RELATED APPLICATION

[0001]   This application claims the benefit of U.S. Patent Application Serial No. 60/418,519, filed 10/15/2002.

BACKGROUND OF THE INVENTION

[0002]   The use of self-limiting chemical reactions to sequentially grow monolayers of transition metals will positively impact many and diverse applications. For example, among the applications for metal atomic layer deposition (ALD) are noble metal catalysts on rough electrode and mesoporous bulk materials, Cu seed layers for the electrochemical deposition and chemical vapor deposition of Cu, conformal adhesion layers to Cu metallic overlayers and alkylthiolate self-assembled monolayers. Palladium is useful as a catalyst in fuel cells and for hydrogenation reactions, gas sensors, and hydrogen permselective membranes. Palladium, like the other noble metals, is rather costly; therefore, a driving force exists to reduce the quantity used as a function of its activity. Atomic layer deposition is an ideal method for extracting the highest performance out of noble metal catalysts with the least cost, since its growth is highly conformal and well controlled. As a result, monolayer-by-monolayer control of growth can take place over complicated geometries and bulk mesoporous supports.

[0003]   In an ALD process, a substrate is exposed sequentially and alternately to at least two mutually reactive reactants. The substrate is heated to a temperature that is high enough to prevent condensation of the reactants but low enough to prevent thermal decomposition of each of the reactants. The substrate is exposed to the first reactant, which is a coordination compound and is chemisorbed onto the surface of the substrate. Ideally this is one monolayer but often less due to precursor desorption (after the pulse is stopped) and steric effects due to bulky ligands as part of the coordination compound used as an ALD precursor. Excess reactant is then evacuated from the deposition chamber so parasitic CVD does not result. Then the substrate is exposed to the second reactant which reacts with the chemisorbed first reactant. The purpose of this pulse is to remove the organic ligand as part of the coordination compound (reactant 1) and reduce the metal ion to its elemental state. When this reaction is complete a submonolayer of the metal results at the substrate surface. This cycle is repeated

until a sufficiently thick film has been deposited onto the substrate. More than two reactants can be used, in particular for the deposition of ternary or more complicated compounds or multilayers. The general technique has been known since 1980, see the review article of Suntola, "Atomic Layer Epitaxy" in: "Handbook of Christal Growth 3, Thin Films and Epitaxy, part B. Growth Mechanisms and Dynamics", by D. T. J. Hurle, Ed. Elsevier, 1994, Chapter 14, p 601-663. Because only a monolayer of the material is deposited per cycle, a sufficient number of cycles need to be executed to achieve the required film thickness. In order to minimize the cycle time without compromising the effectiveness of the purging of the reactor, the volume of the reactor should be minimized and the flow dynamics of the reactor should be optimized.

[0004]   It should be noted that ALD differs from CVD and therefore has different precursor requirements than CVD. ALD is performed in a cyclic fashion with sequential alternating pulses of precursor, reactant and purge gas. The ALD precursor must exhibit self-limiting behavior, such that the precursor is adsorbed on the substrate only up to a monolayer. Because of this self-limiting requirement, only one monolayer or sub-monolayer of precursor is deposited per operation cycle, and additional precursor will not be deposited on the grown layer even when excess precursor is supplied. In CVD, precursor and reactants arrive at the substrate simultaneously with film growth resulting from continuous chemical reactions of precursors on the substrate surface. Uniform and reproducible growth of the film is dependent on maintenance of the correct precursor and reactant flux at the substrate. The growth rate is proportional to the precursor flux at the substrate and to the substrate temperature. Because of the different growth mechanisms, the precursor requirements differ for ALD and CVD. In ALD, the precursor must readily adsorb at bonding sites on the growth surface in a self-limiting mode, and once adsorbed must readily react with co-reactant to form the desired film. In CVD, the precursor and the co-reactants must react appropriately at the substrate surface simultaneously to form the desired film. Thus, many useful CVD precursors are not viable as ALD precursors, and it is not trivial or obvious to select a precursor for the ALD method.

[0005]   Metal ALD to date has had limited success. This is primarily due to the lack of precursor chemisorption on oxide-terminated surfaces and the lack of appropriate reducing agents. The lack of chemisorption with palladium (II) hexafluoroacetylacetonate [PdII(hfac)$_2$] on oxidized Ta, Cu, and P surfaces has been reported by the inventors (Senkevich, *et al.*,

Chem. Vapor Dep. 2002, 8, 189). The inefficacy of hydrogen as a reducing agent on non-metallic surfaces is well established and is attributed to molecular hydrogens lack of polarizability and high bond strength of 435.99 kJ/mol. Alcohols and aldehydes were unsuccessfully used as reducing agents for Cu ALD with CuII(hfac)$_2$ as a precursor (Solanki *et al.*, Electrochem. Solid-State Lett. 2000, 3, 479). Blackburn *et al.* (Chem. Mater. 2000, 12, 2625) also found no growth of Pd via chemical fluid deposition on oxide-terminated surfaces below 230°C. As a result, there is still great interest in developing an ALD technique where metallorganics can be used and deposited on non-noble metal surfaces, for example, polymers, oxidized metals and oxidized barrier layers.

SUMMARY OF THE INVENTION

[0006]   It has been unexpectedly discovered that noble metals including Pd, Pt, Rh, Ru and Ir may be deposited by an ALD process on a variety of substrates. Even more surprisingly, the technique is substrate independent since any surface can be sulfide or thiol terminated via self-assembled chemistry, or plasma-enhanced surface modification.

[0007]   Accordingly, in one aspect, the present invention relates to an ALD process for deposition of a metal selected from Pd, Rh, Ru, Pt and Ir comprising forming a layer comprising the metal on a surface comprising a material selected from W, Ta, Cu, Ni, Co, Fe, Mn, Cr, V Nb, tungsten nitride, tantalum nitride, titanium nitride, dielectrics and activated dielectrics at a temperature ranging from >60°C to <260°C. Forming a layer may include sequentially pulsing into a chamber containing the surface a precursor for the metal and a reducing gas selected from hydrogen, glyoxylic acid, oxalic acid, formaldehyde, 2-propanol, imidazole and plasma-activated hydrogen.

[0008]   In another aspect, the present invention relates to an ALD process for deposition of a metal selected from Pd, Rh, Ru, Pt and Ir including providing a surface comprising a material selected from noble metals, W, Ta, TaN, tungsten nitride, tantalum nitride, titanium nitride, Cu, Ni, Co, Fe, Mn, Cr, V and Nb in a reaction chamber; pulsing a precursor for the metal into the chamber at a temperature ranging from >60°C to <260°C; and pulsing hydrogen gas into the chamber.

[0009]   In yet another aspect, the present invention relates to an ALD process for deposition of a metal selected from Pd, Rh, Ru, Pt and Ir including providing a surface comprising a material selected from noble metals, W, Ta, Cu, Ni, Co, Fe, Mn, Cr, V Nb, tungsten nitride,

tantalum nitride, titanium nitride, dielectrics and activated dielectrics in a reaction chamber at a temperature ranging from >60°C to <260°C; pulsing a precursor for the metal into the chamber; and pulsing into the chamber a reducing gas selected from glyoxylic acid, oxalic acid, formaldehyde, 2-propanol, and imidazole.The activated dielectric surface may include thiol, sulfide, tetrasulfide, phosphine, phosphide or amine groups.

[0010]   In yet another aspect, the present invention relates to an ALD process for deposition of a metal selected from Pd, Rh, Ru, Pt and Ir including providing a substrate in a reaction chamber; pulsing a precursor for the metal into the chamber at a temperature ranging from >60°C to <260°C; and pulsing plasma-activated hydrogen gas into the chamber.

[0011]   For any of these processes, the precursor is preferably a metal β-diketonate compound, more preferably, a metal-hfac compound. Specific examples of preferred precursors for all of the processes are $Pd(hfac)_2$, $Ru(hfac)_2$, $Rh(hfac)_2$, $Pt(hfac)_2$, $Ir(hfac)_2$, $Ir(acac)_2$, $Pd(tmhd)_2$, $Ru(tmhd)_2$, $Rh(tmhd)_2$, $Pt(tmhd)_2$, and $Ir(tmhd)_2$.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012]   Figure 1 – The chemical structures of the Pd ALD precursor and novel reducing agent used in this study.

[0013]   Figure 2 – The structure of the tetrasulfide SAM and Ir substrates used in this study.

[0014]   Figure 3 – The sequential growth of Pd ALD films has a function of the number of cycles for $Pd^{II}(hfac)_2$ pulsed separately with H_2. The films at 130 °C show less growth with more cycles due to the desorption of $Pd^{II}(hfac)_2$ on Pd versus Ir. The ALD process. Pd is not deposited monolayer by monolayer due to the presence of bulky organic ligands.

[0015]   Figure 4 – The Pd 3d XPS spectra for 60 Å of Pd deposited on the tetrasulfide SAM and for 55 Å of Pd deposited on Ir. The peak position of the Pd $3d_{5/2}$ peak is slightly shifted from elemental Pd, which might be attributed to charge referencing or slight chemical contamination from the dissociation of the hfac ligand.

[0016]   Figure 5 – The C 1s XPS spectra for the Pd ALD films deposited on the tetrasulfide SAM and Ir surfaces. The high binding energy shoulder on the peak associated with the C-C or adventitious bonding is associated with $-CF_x$, C=O, or C-O bonding due to the dissociation of the hfac ligand.

[0017]   Figure 6 – The F 1s XPS spectra for the Pd ALD films deposited on the tetrasulfide SAM and Ir surfaces. The peak position of the spectra is correlated with the fluorine being associated with carbon.

[0018]   Figure 7 - S 2p XPS spectrum showing the Pd-S interfacial reaction between $Pd^{II}(hfac)_2$ and the tetrasulfide SAM.

[0019]   Figure 8 – The Ir 4f XPS spectra showing the Pd-Ir interfacial reaction between $Pd^{II}(hfac)_2$ and the Ir surface. The binding energy shift is only obvious for the 240 cycle Pd film because only the interfacial chemistry contributes to the Ir signal.

[0020]   Figure 9 – Reflection high energy electron diffraction (RHEED) images and spectra for 55 Å of Pd on Ir (top), 60 Å of Pd on tetrasulfide SAM (middle), and the 150 Å Ir substrate (bottom). The Pd on Ir exhibits a higher quality texture than the Ir substrate itself. However, the Pd on the tetrasulfide SAM is nearly random, which is attributed to the higher temperatures needed to achieve the Pd seed layer.

[0021]   Figure 10 – Proton Nuclear Magnetic Resonance Spectroscopy of the glyoxylic acid reducing agent before (bottom spectrum) and after (top spectrum) dehydration in vacuum (10 sccm Ar carrier and 10^{-4} Torr base pressure) at 60 °C for 60 min. The broad peaks at 7.2 and 8.5 ppm are attributed to a proton exchange mechanism between glyoxylic acid and water. When the peak is at higher chemical shifts it is more associated with the acid than free water.

DETAILED DESCRIPTION OF THE INVENTION

[0022]   Metals that may be deposited by the ALD processes of the present invention include Pd, Pt, Ru, Rh and Ir, and particularly Pd.   Suitable precursors for the metals sublime without decomposition, exhibit self-limiting chemistry and are stable at deposition temperatures. Further, they should be susceptible to decomposition on the substrate and fragments of the ligand(s) should be removable there from. Precursors are typically coordination compounds based on bidentate ligands such as β-diketonates or carboxylates. The β-diketonates are particularly useful. Examples of β-diketonate ligands include hfac, acetylacetonate (acac), tfac, fod, and tetramethylheptanedionate (tmhd). Adducts of the coordination compounds with Lewis bases may be also be utilized. Examples of Lewis bases that may be suitable include pyridine, 4,4' bipyridyl, imidazole, ammonia, n-propanol, n-butanol, and methanol. Examples of coordination compounds that are typically suitable as

precursors include $Pd(hfac)_2$, $Pt(hfac)_2$, $Ru(hfac)_2$, $Rh(hfac)_2$, $Ir(hfac)_2$, and $Ir(acac)_2$. Precursors for palladium include palladium (II) hexafluoroacetylacetonate, palladium (II) tetramethylheptanedionate, palladium (I) hexafluoroacetylacetonate with 2-methylallyl ligand, palladium (I) acetylacetonate with 2-methylallyl ligand and palladium (II) hexafluoroacetylacetonate with Lewis base adducts and palladium (II) carboxylate complexes

[0023] Deposition temperatures range from >60°C to <260°C, and preferably, from about 80°C to about 200°C . The temperature is typically chosen with a particular precursor in mind, especially since, as noted above, the precursor must be stable at the deposition temperature. The reducing agent used also determines the deposition temperature. For catalytic processes using hydrogen or activated hydrogen as the reducing agent, temperatures typically range from about 60°C to about 130°C, preferably from about 80°C to about 100°C. For organic reducing agents, deposition temperatures are much higher, typically >150°C, and in some cases, >200°C.

[0024] Suitable reducing agent in gas form, or reducing gases, for use in the processes of the present invention are able to remove the organic ligand that is a part of the coordination compound and reduce the metal ion to its elemental state. These include, for appropriate substrates or surfaces, hydrogen, organic reducing agents and plasma-activated hydrogen.

[0025] Hydrogen is capable of reducing the metal ions on surfaces including noble metals (Ru, Rh, Pd, Os, Pt), oxide-terminated metallic surfaces where the oxide can be removed with a pretreatment (W, Ta, tungsten nitride, tantalum nitride, titanium nitride) and metallic surfaces where a transmetallation reaction can occur (Cu, Ni, Co, Fe, Nm, Cr, V, Nb). For such a reaction to occur, the metal being deposited must be more noble than the substrate, the substrate can not be terminated with an oxide, and the coordination compound that is a product of the reaction (e.g., $Cu(hfac)_2$ from $Pd(hfac)_2$ on Cu), must be stable.

[0026] Where it is desired to deposit a metal layer on a surface or substrate other than the above, organic reducing agents or gases or plasma-activated hydrogen may be used. Activated hydrogen is substrate-independent because the plasma creates atomic hydrogen and hydrogen ions that are energetic and can reduce metal ions on essentially any surface. In addition, the metal layer produced is of high chemical quality. Examples of means for activating hydrogen include radiofrequency (RF) or microwave plasmas, either near-surface

or remote, such as capacitively coupled plasmas, inductively coupled plasmas, microwave cavity plasmas, and electron cyclotron resonance plasmas.

[0027]   Organic reducing agent such as glyoxylic acid, oxalic acid, formaldehyde, 2-propanol and imidazole may be used for noble metals, W, Ta, tungsten nitride, tantalum nitride, titanium nitride Cu, Ni, Co, Fe, Nm, Cr, V, and Nb surfaces, and also for activated dielectric surfaces. Dielectric substrates which can be activated toward ALD at the surface include metal and silicon oxides, CVD polymers such as the parylenes, hybrid organic-inorganic composites and oxide-terminated metals, although almost any surface may be activated using an appropriate technique. Such materials may be low κ dielectrics, high κ dielectrics, metal oxides, silicon oxides, hybrid materials composed of organic and inorganic constituents, polymeric materials, and diffusion barrier materials.The dielectric surface may be activated by attaching functional groups containing sulfur, phosphorous or nitrogen using solution or vapor deposition techniques. Essentially any form of sulfur that may be attached to the surface of the substrate may be used, and particularly sulfur in the form of thiol (-SH), thio ether (-S-), sulfide (-SS-), tetrasulfide (-SSSS-) groups may be used. Phosporous is typically in the form of phosphine or phosphide groups. Nitrogen is typically in the form of primary, secondary, tertiary and quaternary amine functionality. For example, a self-assembled monolayer or multilayer (SAM) may be formed at the surface of the substrate using multifunctional silanes. These techniques are well known and have been described in the literature. Self-assembled monolayer/multilayers (SAM's) grow in an ordered structure due to the chemical anisotropy that exists within the molecules. Three types of SAM's are common: alkyl thiolate SAM's (on Ag, Au, and Cu) (Laibinis et al., *J. Am. Chem. Soc.* 113:7152-7167 (1991)), trichlorosilyl SAM's (on hydroxylated surfaces) (Vuillaume et al., *Appl. Phys. Lett.* 69(11):1646-1648 (1996)), and trialkoxysilyl SAMs (on hydroxylated surfaces) (Dressick et al., *J. Electrochem. Soc.* 141(1):210-220 (1994)). Namely, the alkylthiolate, trichlorosilyl, and the trialkoxysilane groups have significantly different reactivity than terminal groups on the other side of the SAM molecule, e.g. pyridine (-C_5H_4N), methyl (-CH_3), phenyl (-C_6H_5), and mercaptan (-SH), and thus the SAM molecule will not react with itself. SAMs anchored by trichlorosilyl or trialkoxysilyl groups may be used with surfaces having surface hydroxy groups. For example, the surface of the native oxide of Si(100) is reactive with chloro- or alkoxy-silanes. For materials that do not possess surface hydoxy functionality, such as barrier layers, the surface may be hydroxylated in a

separate step prior to forming the SAM. These techniques are also described in US-2002-0182385.

[0028]   In some cases, where the deposition temperature with the organic reducing agents is higher than desired, e.g. ~200 °C, then only a seed layer of Pd is deposited using the organic reducing agent since the deposition rate of noble metal maybe be prohibitively slow. Once the seed layer is deposited, the temperature may be lowered to, for example, 80 °C and the ALD growth of the metal layer resumes at a much faster rate. This rate difference is due to significant desorption of the metallorganic that takes place at higher temperatures due to low interaction energy between the precursor and the freshly created metal surface.

[0029]   The purge time, that is, the time between pulse A (precursor) and pulse B (the reducing agent), should be large enough that no parasitic CVD occurs. This typically depends on the conductance of the vacuum system and the pumping speed of the vacuum pump stack. A minimum of 10 s is frequently needed but this can be reduced to ~1 s. The reducing agent (pulse B) pulse duration is the same as pulse A (precursor).

EXPERIMENTAL

Palladium ALD on Ir:

[0030]   The use of Ir as an ALD substrate accomplishes two things. First, it has been established that $Pd^{II}(hfac)_2$ preferentially chemisorbs on Ir. Second, Ir is known to dissociate molecular hydrogen, which acts as a reducing agent and removes the hfac ligands from the $Pd^{II}(hfac)_2$ metallorganic. Further, it is important to establish two experimental findings to make the ALD process viable. First, the precursor (or metallorganic) should be able to be sublimed without decomposing. This can be undertaken with thermogravimetric analysis. Fortunately, $Pd^{II}(hfac)_2$ has already been shown to sublime without decomposing. Second, the metallorganic should not decompose at the substrate's surface until temperatures that exceed the deposition temperature of the metal. This has been shown previously with $Pd^{II}(hfac)_2$ to be 230 °C on Ir and on a unspecified surface.

[0031]   As a result of the above work the processing window for the ALD of Pd is between 60 °C and 260 °C. The lower limit is due to the condensation of the precursor and the upper limit is due to its thermal decomposition (non-self-limiting growth). The substrate structure of Ir

and the tetrasulfide SAM is shown in Figure 2 and explained in more detail in the experimental section. Figure 3 shows the thickness of the ALD Pd thin films as a function of the number of cycles. The areal density of the Pd films was obtained by RBS and then converted to a thickness value by: $1 \text{ Å} = 6.80 \times 10^{14}$ atoms/cm^2 obtained from palladium's density and molecular weight.

[0032] As can be seen from Fig. 3, the Pd films grown at 130 °C do not exhibit a linear relationship between film thickness and the number of cycles. This paralinear growth is attributed to the difference in bond energies between Ir-Pd^{II}(hfac)$_2$ and Pd-Pd^{II}(hfac)$_2$. The atomic polarizabilities of Ir and Pd are 7.6 ± 1.9 Å^3 and 4.8 ± 1.2 Å^3 respectively. The larger polarizability helps to stabilize the van der Waals forces between the Ir surface and the Pd^{II}(hfac)$_2$ metallorganic. The change between the initial growth (Ir-Pd^{II}(hfac)$_2$) and the subsequent growth (Pd-Pd^{II}(hfac)$_2$) does not occur until nearly ~10 Å due to the growth mechanism of ALD Pd via Pd^{II}(hfac)$_2$. It should be realized that monolayer-by-monolayer deposition of metallic atoms does not occur but instead the monolayer deposition of, for example, Pd^{II}(hfac)$_2$ occurs assuming no desorption. The primary reason for the lack of monolayer-by-monolayer growth is due to the large size of the organic ligands associated with the metallorganic precursor.

[0033] At 80 °C the vapor pressure of Pd^{II}(hfac)$_2$ is much lower and the Pd-Pd^{II}(hfac)$_2$ bond is strong enough that little desorption occurs. However, when Pd is grown on Ir via Pd^{II}(hfac)$_2$/H$_2$ an incubation period is consistently observed. It is known that H$_2$ has a very high reactivity with Pd^{II}(hfac)$_2$ and therefore this observation is likely attributed to carbon residing at the Ir surface. After the prerequisite number of cycles of H$_2$, the carbon can be adequately cleaned and Pd ALD can commence. The adventitious carbon on the Ir surface was observed with XPS (not shown) and was significantly greater then on, for example, a SiO$_2$ surface. Further, as the temperature of the substrate is raised, the ability of hydrogen to clean the Ir surface should increase.

Palladium ALD on Ir and the tetrasulfide SAM (XPS):

[0034] Ex situ X-ray photoelectron spectroscopy is used to investigate the chemical quality of the Pd ALD films. In particular, comparisons are made for Pd deposited on Ir versus the tetrasulfide SAM. The primary difference between the two types of depositions is that a Pd 'seed' layer is deposited via ALD on the tetrasulfide SAM at temperatures >200 °C, where

glyoxylic acid is active, and then Pd is deposited by the $Pd^{II}(hfac)_2/H_2$ process at 80 °C used with Ir. The process is outlined in Fig. 2 and explained in the Experimental section. Glyoxylic acid was chosen as an effective metallorganic reducing agent due to its use as an electroless Cu reducing agent and its thermal dissociation to form CO_2 and H_2CO at temperatures greater than 200 °C.

[0035]   Figure 4 shows the Pd 3d XPS spectra for Pd deposited on Ir and on the tetrasulfide SAM. The Pd $3d_{5/2}$ peak for the tetrasulfide SAM surface is referenced to carbon (C 1s peak) at 285.0 eV from previous work. The Pd $3d_{5/2}$ peak for the Ir surface is referenced to adventitious carbon at 284.6 eV for the C 1s peak. The value for adventitious carbon on Ir was determined with a separate experiment. This measurement must be done with care since the tail of the Ir $4d_{5/2}$ peak at 297 eV can interfere with the C1s peak at 284.6 eV. As a result, quantitative results are hard to come by, but the peak position is easily obtainable.

[0036]   The peak positions of both the Pd $3d_{5/2}$ peaks in Fig. 4 at 335.7 eV are close to what has been previously established in the literature for elemental Pd. Elemental Pd has been shown to have a Pd $3d_{5/2}$ binding energy of 334.8, 335.3, and 335.4 eV. The slight shift to larger binding energies may be attributed to charge referencing or slight contamination from the dissociation of the hfac ligand. However, the relationship between the chemical contamination and the binding energy shift may be less important since the Pd deposited on the tetrasulfide SAM has higher contamination levels (C and F) in contrast to the Pd deposited on Ir but still has the same Pd 3d binding energy.

[0037]   The C 1s and F 1s XPS spectra of Pd deposited on the tetrasulfide SAM and Ir surfaces are shown in Figures 5 and 6. The Pd deposited on the tetrasulfide SAM has significantly higher levels of carbon and fluorine compared to the Ir substrate. This is likely caused by the high temperatures (>200 °C) needed to deposit the Pd seed layer with glyoxylic acid. Higher temperatures favor a greater degree of ligand dissociation, which is problematic with the β-diketonate metallorganics. Both C 1s spectra show evidence of CF_X, C=O, or C-O bonding due to dissociation from the original hfac ligand. Much of the carbon that exists in Fig. 6 is attributed to adventitious sources existing at the top of the Pd deposit due to ex situ analysis. Proper chemical analysis of the Pd ALD films would be better undertaken in situ; however, experimental difficulties preclude this set up at this time.

[0038] Golub *et al.* have shown that the peak position of the F 1s peak is correlated to atomic percent fluorine that exists in polymer repeat units. Poly(tetrafluoroethylene) (PTFE) has a atomic percent fluorine of 67% and a corresponding binding energy of 689.2 eV. The same – CF$_2$- group has a binding energy in the C 1s spectra of 290.0 eV to 291.4 eV. Lin *et al.* showed that physisorbed Pd^{II}(hfac)$_2$ on a clean Cu surface at 120 K had a F 1s binding energy of 688.2 eV. After annealing the physisorbed Pd^{II}(hfac)$_2$ at 473 K they saw the formation of a new peak at 682.9 eV. However, the fluorine associated with the Pd ALD films in Fig. 6 are at 688.9 eV (on tetrasulfide SAM) and 689.5 eV (on Ir), which may indicate a loss of carbonyl groups from the hfac ligand. Also, it should be noted that carbon bonded fluorine typically has larger F 1s binding energies as compared to metal fluorides and the binding energies of the F 1s spectra in Fig. 6 is consistent with the former.

Interfacial interactions between Pd^{II}(hfac)$_2$ and the tetrasulfide SAM and Ir surfaces:

[0039] It was established previously that Pd^{II}(hfac)$_2$ interacts weakly or not at all with hydroxyl or oxygen terminated surfaces. Further, weak van der Waals interactions are not strong enough to make ALD possible. As a result, chemisorption needs to exist between Pd^{II}(hfac)$_2$ and the tetrasulfide SAM and Ir surfaces. That chemisorption exists means that interfacial Pd-S and Pd-Ir bonding should be evident. In order to see such bonding in the XPS spectra, for example, the Pd-S signal should be large relative to the C-S or S-S bonding, if the S 2p spectrum is used for analysis.

[0040] Figure 7 shows the S 2p spectrum for a monolayer of Pd^{II}(hfac)$_2$ deposited on the tetrasulfide SAM surface (Fig. 2). The tetrasulfide SAM has a peak at 164.1 eV in the S 2p XPS spectrum, which has previously been established. After pulsing Pd^{II}(hfac)$_2$ over the surface, chemisorption is evident and a significant binding energy shift occurred in the S 2p spectrum as shown in Fig. 8. The composite S 2p peak exists at 163.1 eV, whereas the deconvoluted spectra has two peaks, one associated with the S 2p$_{3/2}$ peak at 162.7 eV and one at 163.9 eV associated with the S 2p$_{1/2}$ peak. The spin orbital splitting is 1.18 eV between the S 2p peaks. The shift in the Pd 3d spectrum for one monolayer versus a 60 Å film is not significant.

[0041] The Pd ALD films deposited on Ir are slightly different than the ones deposited on the tetrasulfide SAM because the Ir film is ~150 Å versus on just a monolayer for the sulfur terminated SAM. As a result, interfacial bonding is only evident in Figure 8 for the 31 Å Pd

film that was deposited with 240 cycles at 130 °C. Before that point the Ir-Ir bonding overwhelms the Pd-Ir bonding and this peak is convoluted in the Ir 4f spectra. The Ir $4f_{7/2}$ peak is centered at 60.91 eV, which is literature value. The Pd-Ir interfacial bond is centered at 60.72 eV. No literature value exists for this bonding but IrSi bonding has been reported at 60.70 eV, which may be similar to Pd-Ir.

Reflection High Energy Electron Diffraction (RHEED):

[0042]   The structure of the Pd ALD films is most easily obtained by using a RHEED camera under ultra high vacuum (UHV) conditions. RHEED is sensitive to the structure of angstrom thick metallic films, whereas conventional X-ray diffraction is not appropriate due to the small X-ray cross-section.

[0043]   Figure 9 shows the RHEED images and the corresponding spectra of Pd on Ir, Pd on the tetrasulfide SAM, and the Ir substrate itself obtained from digitizing the images. The ~150 Å Ir thin film thermally evaporated on hydrogen-terminated Si(100) exhibits some slight (111) orientation but nearly exhibits random texture. The calculated lattice constant is 3.81 ± 0.06 Å based on a d-spacing of 2.86 ± 0.04 Å for the (111) plane, which is near the literature value of 3.839 Å.

[0044]   Despite the nearly random texture of the Ir substrate, the 55 Å Pd ALD film deposited on it has much preferred (111) texture. The lattice constant is 3.8 ± 0.1 Å based on the (111) d-spacing. The grain size is ~60 Å, which is very similar to the thickness of the Pd film. Also, it has a texture spread of ~70° at the surface and ~40° in the bulk of the film. The high quality Pd ALD film would be expected for the deposition of a metal on a higher surface free energy metal that is relatively smooth, ~10 Å RMS (from AFM measurements).

[0045]   The Pd ALD film grown on the tetrasulfide SAM possesses very small grains and has nearly random texture. This is uncharacteristic of a metal film that exhibits monolayer wetting as shown previously. However, the difficulty that arises with the use of $Pd^{II}(hfac)_2$ is the high volatility it possesses at low temperatures, e.g. 1 Torr at 60 °C. Further, the hfac ligand shows some instabilities even at room temperature and as the dosing or substrate temperature is raised the dissociation of the hfac ligand becomes worse. As previously explained, glyoxylic acid is only effective as a reducing agent at temperatures greater than 200 °C. Therefore, the processing method developed here is more suitable for lower vapor

pressure metallorganics that do not dissociate at the deposition temperatures needed to undertake ALD for their respective metal.

Chemical Analysis of Glyoxylic Acid:

[0046]   Glyoxylic acid was used here to deposit a Pd seed layer via ALD on top of the tetrasulfide SAM. After the seed layer is deposited, Pd can be deposited via H_2 at low temperatures where the growth rate per cycle is higher. The preliminary experiments showed that glyoxylic acid is only effective as a reducing agent above 200 °C, which is the temperature where it thermally decomposes. At lower temperatures, ~200 °C, a 5:1 ratio exists between CO_2 and formaldehyde for the decomposition products. As the temperature is raised a lower ratio is evident but CO_2 is always the dominant species. Nevertheless, glyoxylic acid is an effective reducing agent since it decomposes cleanly to yield oxidation products and electrons available for reduction reactions with the metallorganic.

[0047]   The as-received glyoxylic acid is a hydrate and water is known to dissociate β-diketonate metallorganics. Proton Nuclear Magnetic Resonance Spectroscopy (^{1}H-NMR) was used to analyze the glyoxylic acid as-received and after dehydration to ensure that glyoxylic acid was utilized as a reducing agent rather than effects caused by the presence of water. Figure 10 shows the ^{1}H-NMR spectra for the glyoxylic acid before and after dehydration under vacuum heating to 60 °C for 60 min. There are four peaks in the proton spectra for glyoxylic acid dissolved in d_6-acetone: The tetramethylsilane reference peak at 0 ppm, 2.1 ppm acetone (impurity in the d_6-acetone), 5.3-6.1 ppm glyoxylic acid, and a broad peak attributed to proton exchange between the glyoxylic acid and water. Two items are apparent from the ^{1}H-NMR spectra. The integrated area between the broad peak at 7.2 ppm for the as-received sample and the group of peaks at 5.3-6.1 ppm associated with glyoxylic acid is 2.9:1. In contrast, the ratio for the dehydrated sample is 0.8:1. Second, the peak associated with proton exchange shifts from 7.2 ppm (FWHM = 17.1 Hz) to 8.5 ppm (FWHM = 113 Hz). The conclusions to be made from these observations are that much less water exists in glyoxylic acid sample without taking into consideration the water in the d_6-acetone and the water adsorbed after the sample was dehydrated. Further, the protons are much more associated with the acid than 'free' water after dehydration. This last conclusion comes from the larger chemical shift for the dehydrated sample. As a result, glyoxylic acid is effective as a reducing agent, there is little associated water, and therefore water plays a very little role in the removal of the hfac ligands from the $Pd^{II}(hfac)_2$ metallorganic.

[0048] The thicknesses of the Pd ALD films were measured as a function of the number of ALD cycles via Rutherford Backscattering Spectrometry. At a deposition temperature of 130°C the relationship was not linear due to the high volatility of $Pd^{II}(hfac)_2$ or in other words its high desorption rate from the freshly created Pd surface. However, at lower temperatures (80°C) the desorption rate is not significant and linear growth is observed. The Pd ALD films were also characterized by X-ray Photoelectron Spectroscopy and Reflection High Energy Electron Diffraction. The films grown on the tetrasulfide SAM had a higher levels of carbon and fluorine contamination attributed to the high temperature need to deposit the Pd seed layer. This was related to the dissociation of the hfac ligand. When the films were grown on Ir the contamination levels were lower due to the temperature dependence of the hfac dissociation. Further, the films grown on Ir exhibited (111) texture with a grain size of ~60 Å for a 55 Å thick film. In contrast, the Pd films grown on the tetrasulfide SAM showed very small grains with nearly random texture. This relative poor structure, as compared to the Pd film grown on Ir, was attributed to the dissociation of the hfac ligand thus allowing fluorine and carbon contamination at the Pd seeded surface.

EXPERIMENTAL

[0049] Two surfaces were used for the atomic layer deposition of palladium as shown in Figure 2. 150 Å of Ir (99.95% Alfa Aesar, Ward Hill, MA) was electron beam deposited onto a Si (100) wafer. The other surface was a tetrasulfide terminated self-assembled monolayer solution grown on the native oxide of Si (100) via bis[3-(triethoxysilyl)propyl]-tetrasulfide (>97% Gelest Inc., Morrisville, PA). The details of the growth and characterization of this monolayer has been published previously.

[0050] A custom-built vacuum chamber with computer controlled gas flow was used for the atomic layer deposition of palladium via $Pd^{II}(hfac)_2$. The base pressure of the vacuum system is 5.0×10^{-4} Torr with the use of a roots blower/direct drive roughing pump (Leybold RUVAC WS/WSU 151 and TRIVAC D25 BCS (hydrocarbon prepped)) and a 3.7 L foreline trap (bronze gauze) to prevent oil backstreaming. The vacuum chamber is a warm walled to prevent condensation of the $Pd^{II}(hfac)_2$ precursor. Further, pneumatic valves can turn off or turn on the gas flow and mass flow meters can control the flow of gases into the system under steady state conditions.

[0051]   Two types of depositions were undertaken, one on a noble metal surface (Ir) and one on a tetrasulfide SAM. The depositions (outlined in Fig. 2) on Ir were undertaken at a deposition temperature of 80 ± 4 °C or 130 ± 4 °C and a $Pd^{II}(hfac)_2$ sublimation temperature of 49.8 ± 0.2 °C. The deposition chamber walls were kept at 60-65 °C and the lines between the sublimation tube and the deposition chamber at 90-95 °C to ensure no cold spots existed to condense $Pd^{II}(hfac)_2$. During each experiment, 30 sccm Ar (99.999% Air Products) was flowed as a purge gas, 10 sccm Ar as a carrier gas for $Pd^{II}(hfac)_2$, and 8.0 sccm H_2 (99.999% Air Products) as a reducing gas. The pulse sequence was 5 s of $Pd^{II}(hfac)_2$ followed by 10 s of 'dead time' with just 30 sccm Ar flowing as a purge gas, and then 20 s of H_2. The number of cycles per deposition varied from 8 to 240 for Pd ALD on Ir.

[0052]   The depositions on the tetrasulfide SAM were slightly different due to the inefficacy of glyoxylic acid (Alfa Aesar, MA) as a reducing agent below 200 °C and the high rate of desorption of $Pd^{II}(hfac)_2$ on Pd at temperatures above 200 °C due to its high vapor pressure and low interaction energy with Pd. This behavior may be followed in terms of Langmuir kinetics. As a result, these depositions consisted of two parts. The first part consisted of depositing a 'seed' layer of Pd, where $Pd^{II}(hfac)_2$ was pulsed for 5 s alternatively with 60 s pulses of glyoxylic acid (sublimation temperature 60 ± 2 °C and 15 sccm Ar carrier). As with all of the depositions a 10 s dead time was used. It took 120 cycles to deposit the 'seed' layer of Pd, after that point the $Pd^{II}(hfac)_2/H_2$ process was used at 80 °C for 120 cycles more.

[0053]   The Reflection High Energy Electron Diffraction Images (RHEED) images were taken with a 15 keV electron beam source that produces a 100 μm diameter spot size. The pressure of the stainless steel chamber was $\sim 1 \times 10^{-9}$ Torr. The high-energy electron beam was incident at 1° from the sample plane. The diffracted electrons pass through two metal retarding grids before striking the phosphor-coated screen, which is imaged using a 16-bit Princeton Instruments CCD camera. The Nuclear Magnetic Resonance Spectroscopy (FT-NMR) work on the analysis of the water in the glyoxylic acid was undertaken on a Varian Unity INOVA 300 (300 MHz). ^1H-NMR spectra were undertaken on dehydrated and as-received glyoxylic acid with 8 scans with a pulse width of 8 μs at 90 ° in d_6-acetone with 1v/v% tetramethylsilane (TMS) as a proton standard.